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PREPARATION AND INVESTIGATION OF AMORPHOUS GALLIUM

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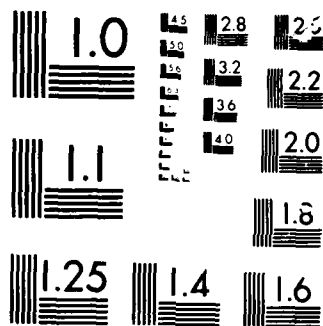
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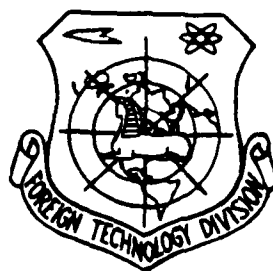
## FOREIGN TECHNOLOGY DIVISION



PREPARATION AND INVESTIGATION OF AMORPHOUS GALLIUM ARSENIDE FILMS

by

Wu Rulin, Chen Kunji, and Yang Zoya



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# PREPARATION AND INVESTIGATION OF AMORPHOUS GALLIUM ARSENIDE FILMS

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## ABSTRACT

A new method for the preparation of a-GaAs films -- Plasma Enhanced Chemical Transport Deposition (PECTD) is described. The experimental results indicate that a bright smooth surface, a nearly stoichiometric composition and a good reproducibility of the a-GaAs films could be obtained if proper technological conditions were selected and controlled. The growth mechanism of PECTD is also discussed.

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*Thin Film of Arsenic*

## 1. INTRODUCTION

Amorphous semiconductor is a new type of electronic material. Due to its special physical properties, it is paid more and more attention to in both China and other countries. Recently the research of the element amorphous semiconductors such as a-Si, a-Ge, and the sulphide series glass materials has entered quite intensive stages. These materials have also been applied to some devices. But the study of amorphous III-V component materials is just beginning. The reason for this is that the randomness of structure and content of this type of amorphous materials are far more complicated than the element semiconductors [1]. Until now only the basic physical properties of thin film materials

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\*Refers to pagination of foreign text.

such as a-GaAs and a-GaP have been studied. According to the results of optical absorption study, at the maximum position of the solar spectrum ( $\sim 2.5$  eV), the absorption of a-GaAs is 25 times that of c-GaAs, and is 2 times that of a-Si:H. Therefore it is estimated that an a-GaAs material might obtain application in photovoltaic devices. Recently it was reported that Japan had increased the efficiency of an a-Si solar cell to 15% by adding a layer of a-GaAs. Besides that, considering the transport properties of electrons in an a-GaAs material, the possibility of making an insulating electrode of MIS structure GaAs field effect transistor is being studied.

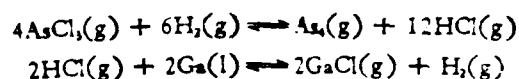
Most foreign countries use evaporation and sputtering to prepare a-GaAs thin film material [2,3], and glow discharge is also used to prepare this material [4]. We are the first to use the new method of Plasma Enhanced Chemical Transport Deposition (PECTD) to prepare this material. By the rigorous control of processing parameters in this method, we have successfully prepared an a-GaAs thin film material with nearly stoichiometric composition. We also have studied the structure and composition by using a transmission electron microscope, spectroscopy, and infrared spectrometer. In this paper we also make an initial analysis on the growth mechanism.

## 2. DEPOSITION PRINCIPLES AND EXPERIMENTAL ARRANGEMENT

Vapor epitaxy is the most common method to prepare a c-GaAs epitaxy layer and a Ga/AsCl<sub>3</sub>/H<sub>2</sub> system is widely used. A typical vapor epitaxy system consists of two temperature zones. The higher temperature zone is the source zone ( $\sim 850^\circ\text{C}$ ), and the lower temperature zone is the deposition zone ( $\sim 750^\circ\text{C}$ ). Ga is transferred into a vapor phase

in the source zone in the form of GaCl. When it enters the deposition zone, GaAs is formed by the chemical reaction in an As<sub>4</sub> gas environment. In this reaction-deposition system, because the temperature is too high, no a-GaAs material can be obtained. If the temperature in the deposition zone is decreased enough, then it is possible to obtain a-GaAs. But unfortunately the reaction speed of GaCl and As<sub>4</sub> will decrease along with the decrease of temperature [5]. In order to solve this problem, we suggested using the energy of plasma to assist the reaction of GaCl and As<sub>4</sub>. This is the starting point of the PECTD method. Therefore the PECTD method is similar to the vapor phase epitaxy method and also uses Ga/AsCl<sub>3</sub>/H<sub>2</sub> and a two temperature zone system. The difference is that the temperatures in the source and deposition zones are lowered a little and plasma produced by a radio frequency electrical field is introduced into the deposition zone.

In the PECTD system, the chemical reactions in the deposition zone are as follows.



Under the influence of the gradient of pressure and temperature, all the gases in the source zone are transferred to the deposition zone. When a suitable radio frequency electrical field is added to the deposition zone, the heat electrons in the reaction chamber will collide with these gas molecules and make them excited, decomposed, or ionized to form plasma. With the control of the gas pressure and power of the radio frequency field, this plasma will promote the reaction of GaAs. The reaction process is as shown in Figure 1.



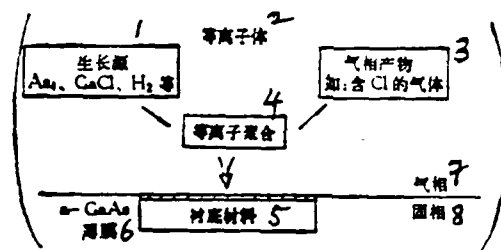


Figure 1. The reaction process of GaAs in the PECTD system.

Key: 1) source; 2) plasma; 3) gas phase products; 4) synthesis of plasma; 5) substrate; 6) thin film; 7) gas phase; 8) solid phase.

In the PECTD system, the source zone offers the necessary gas source for the growth of an A-GaAs thin film, and the synthesis reaction takes place in the deposition zone under certain temperature and electrical fields to form a-GaAs films.

According to the above principles, we made the experimental arrangement as shown in Figure 2.

The whole deposition system is divided into two zones: the source and deposition zones. The temperature required by the chemical reactions in the source is obtained by using a heater. A pair of stainless steel electrodes was installed in the deposition zone for applying radio frequency power and therefore to produce plasma. H<sub>2</sub> is led to the deposition zone for adjusting the gas pressure in the system.

The source of the reaction is the liquid phase AsCl<sub>3</sub> and metal Ga. Both of them have a purity of 99.999%. The pre-disposed Ga source is placed in the source zone

and  $\text{AsCl}_3$  is held in a quartz source bottle and is carried into the source zone by high purity  $\text{H}_2$ .

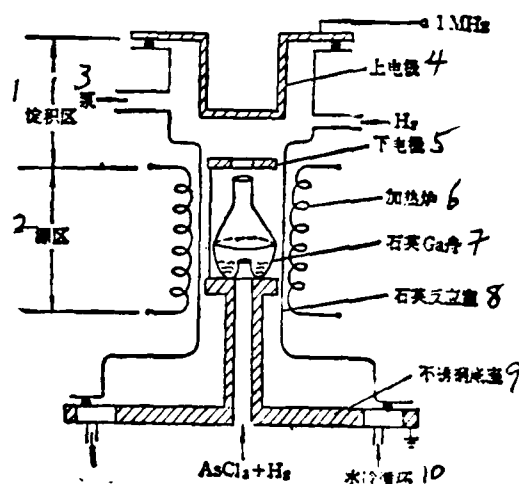


Figure 2. The experimental arrangement of the PECTD method.

Key: 1) deposition zone; 2) source zone; 3) pump; 4) upper electrode; 5) bottom electrode; 6) heating oven; 7) quartz boat of Ga; 8) quartz reaction chamber; 9) stainless steel base; 10) cooling water.

The substrate materials are cleaned cover glass plates, Corning 7059 glass, double-polished c-Si,  $\text{SiO}_2/\text{Si}$ , etc. In order to eliminate the impurities adsorbed on the surface of the substrate, usually the substrates are cleaned by using plasma disposal before the growth of a-GaAs thin films.

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The typical conditions for the film growth are shown in Table 1. In this table,  $I_a/I_g$  is the ratio of the anode current of the radio frequency source to the grid current;  $T_{so}$  is the temperature of the source zone for a-GaAs growth.

Table 1.

电极间距离 <sup>1</sup>	$I_s/I_e$	$T_{so}$	AsCl <sub>3</sub> 源温 <sup>2</sup>	AsCl <sub>3</sub> 流量 <sup>3</sup>	生长气压 <sup>4</sup>
~25mm	80/22	~600°C	0°C	针型阀 2 格 <sup>5</sup>	~20Torr

Key: 1) distance between electrodes; 2) source temperature; 3) flux; 4) gas pressure; 5) 2 readings of the needle-type valve.

### 3. THE STRUCTURE OF a-GaAs THIN FILM

We use D/MAX-rA X-ray diffraction spectroscope and EM-100S electron microscope to determine the amorphous nature of the samples. Figure 3 shows the spectrum of diffraction of GaAs film on the glass substrate. The thickness of the samples is larger than 1  $\mu\text{m}$ ; the parameters of measurement are: voltage of the X-ray tube is 40kV, the current of the tube is 100mA, the grating is  $1^\circ$ - $1^\circ$ - $0.15^\circ$ - $0.45^\circ$ .

In the Figure 3, there are two wide diffraction peaks at the diffraction angle  $2\theta=27^\circ$  and  $48^\circ$ , and this is the typical spectrum of a-GaAs film [6]. In order to further prove the non-crystalline nature of the material, we annealed the sample at  $450^\circ\text{C}$  and in  $\text{N}_2$  environment for half an hour. Then we measured the sample again. The results are shown in Figure 4. Sharp peaks appear at  $2\theta=27.2^\circ$ ,  $45.3^\circ$ , and  $53.6^\circ$ , and they are corresponding to the low index planes of (111), (220), and (311) of crystal GaAs. Therefore the sample crystalized after  $450^\circ\text{C}$  annealing was proved.

Similar results were obtained for a-GaAs samples grown at the c-Si substrate.

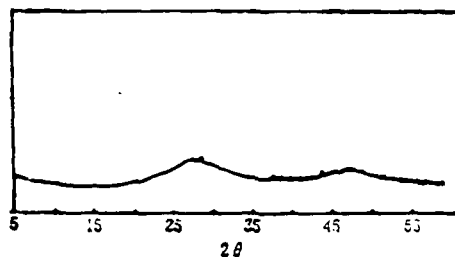


Figure 3. The spectrum of X-ray diffraction of an a-GaAs sample.

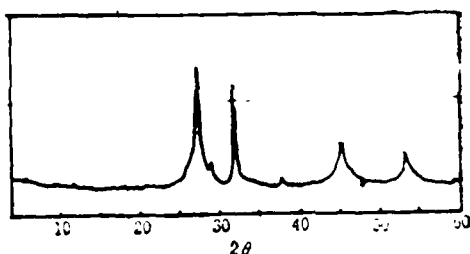


Figure 4. The spectrum of X-ray diffraction of a GaAs sample after annealing.

The average crystalline sizes before and after annealing estimated according to Scherrer formula are shown in Table 2.

Figure 5 and 6 are the image and electron diffraction pattern respectively, by using the same transmission electron microscope. The magnification of Figure 5 is 20,000 and the crystalline size is hard to see. The rings of electron diffraction are similar to the rings of X-ray diffraction and are dispersive.

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Table 2.

衬底材料 1	状态 2	退火前 3	450°C 退火后 4
双抛 c-Si 5		~20 Å	~70 Å
盖玻片 6		~11 Å	~142 Å

Key: 1) substrate material; 2) status; 3) before annealing; 4) after annealing; 5) double-polished; 6) cover glass plate.



Figure 5. The transmission electron microscope image of an a-GaAs sample.

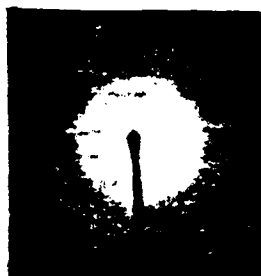


Figure 6. The electron diffraction pattern of an a-GaAs sample.

The above experimental facts show that the thin film prepared with PECTD method has amorphous structure.

#### 4. THE COMPOSITION OF AN a-GaAs THIN FILM

We use an EDAXPVgl00 spectroscopy to study the composition of a-GaAs samples, and a 170SX FTIR infra-red spectrometer to study the bonding status of Ga and As.

Table 3 lists the EDAX data. From the table we see that the a-GaAs samples prepared under typical growth conditions, their Ga and As atomic percentage Ga/As  $\approx 1.10$ , and therefore is nearly stoichiometric. The content of Cl is less than 4 at.%. The reproducibility of the samples is also quite good.

Table 3.

样品编号 /	Ga/As	Cl at.%	生长速率 ( $\text{\AA}/\text{s}$ ) <sup>2</sup>
T15(29)	1.04	2.80	1.3
T15(30)	1.02	2.80	1.5
T15(31)	1.06	2.46	1.0
T15(34)	1.03	2.29	—
T15(35)	1.08	3.01	1.1
T15(36)	1.10	3.90	1.5

Key: 1) No. of sample; 2) growth rate.

Table 4.

样品编号 /	$T_{90}(\text{^\circ C})$	$I_{90}/I_0$	Ga/As
T15(3)	$\sim 630$	50/14	1.14
T15(4)	$\sim 630$	50/14	1.20
T15(43)	$\sim 630$	80/22	1.02
T15(48)	$\sim 600$	80/22	1.10
T15(44)	$\sim 585$	80/22	1.17

Key: 1) No. of sample.

What is different from the results reported in foreign literature is that the a-GaAs thin films prepared by the the PECTD method are usually Ga-rich and not As-rich. This is because the PECTD method is different /359 from the evaporation and sputtering methods and the As atoms in the sample come from  $As_4$  which is a decomposition product of  $AsCl_3$  in the source zone. The decomposition of  $AsCl_3$  is dependent on source temperature  $T_{so}$ . Higher  $T_{so}$  will promote the growth of  $As_4$  and make higher partial pressure of  $As_4$  in the system. Therefore it will depress the density of vacancies of As in the material. Table 4 shows the influence of  $T_{so}$  to Ga/As.

Figure 7 is the Auger spectrum of a-GaAs sample after 25 minutes of  $Ar^+$  bombardment. The instrument used is model PH1550. The spectral lines at 200 ev, 1060 ev, and 1220 ev are corresponding to Cl, Ga, and As.

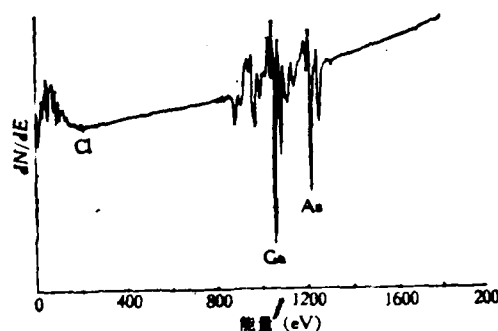


Figure 7. The Auger spectrum of an a-GaAs thin film.

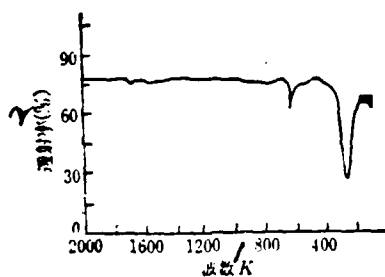


Figure 8. The infra-red spectrum of an a-GaAs thin film sample.

Figure 8 is the infra-red absorption spectrum of an a-GaAs sample. The sample is deposited on a double polished c-Si substrate and the film thickness is about 1  $\mu$ m. There is a strong absorption peak near the wave number of  $250\text{ cm}^{-1}$  and this is the characteristic absorption peak as a result of interaction between the long optical transversal phonon (TO mode) and the infra-red photon. There is a relatively weaker but wider absorption peak at about  $530\text{ cm}^{-1}$  and this is corresponding to the 2TO mode absorption of GaAs. This agrees with the result reported in literature [6].

Until now only the two characteristic absorption peaks were observed in our a-GaAs samples prepared by the PECTD method. We did not yet observe the absorption peaks of Ga-H, As-H, or the corresponding bridge bond [6]. Further work regarding this aspect is being done.

## 5. THE INFLUENCE OF GROWTH ON THE STRUCTURE AND COMPOSITION

An obvious feature of an a-GaAs thin film prepared by the PECTD method is the large influence of the selection and control of the growth conditions on the structure and composition of the samples.

1) Certain substrate temperature is necessary for the growth of a-GaAs thin films. Although we did not intentionally heat the deposition zone, the substrate temperature is about  $150^{\circ}\text{C}$  due to the radiation and conduction of  $T_{\text{so}}$ . If we make the enforced cooling for the substrate while keeping the radio frequency power constant, it will be very difficult to obtain a bright, smooth, dense and continuous film. Most of the films will be polymers,



which easily absorb water, such as  $\text{GaCl}_3$ . The reason is that the partial pressure of  $\text{GaCl}_3$  will increase when  $T_{\text{so}}$  decreases [7] and at low temperatures it will be adsorbed on the substrate and the walls of the reaction chamber. But of course, too high  $T_s$  will lead to the crystallization of a-GaAs thin film.

2) The power of radio frequency at the deposition zone is a key parameter. Table 5 shows the influence of the power (expressed as  $I_a/I_g$ ) on the composition and chemical ratio of a-GaAs thin film.

From this table we know that a larger power of radio frequency can improve the chemical ratio and decrease the content of Cl atoms in the sample.

3) Through the experiment, we found that the position of the substrate and shape of the reaction chamber are important. Figure 9 shows the geometric sizes of our PECTD system.

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Table 5.

样品编号 /	$T_{\text{so}}(^{\circ}\text{C})$	$I_a/I_g$	Ga/As	Cl at. %
T15(45)	~600	110/30	1.11	4.17
T15(47)	~600	80/22	1.23	9.06
T15(46)	~600	50/14	1.26	10.27

Key: 1) No. of sample.

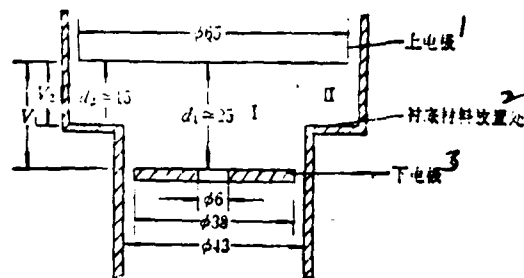


Figure 9. The geometrix sizes of the deposition zone of the PECTD system.

Key: 1) upper electrode; 2) position of substrate; 3) bottom electrode.

If the substrates are put near the upper electrode, usually some polymer which is easy to absorb water will be adsorbed at the sample surfaces. This will lead to samples lacking brightness and the film is fragile and easy to peel off. Only the substrates placed on the stage as shown in Figure 9 will produce bright, smooth, and dense GaAs thin films. The above phenomena can be explained by the Parshen curve.

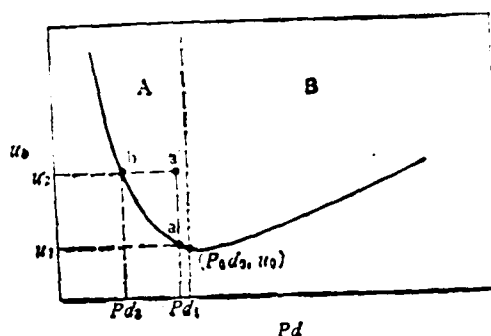


Figure 10. Parshen Curve.

Figure 10 shows the Parshen curve. In this figure  $u_b$  is the maintaining voltage of the plasma,  $p$  and  $d$  are the system pressure and distance between the two electrodes respectively,  $p_0 d_0$  corresponds to the minima of  $u_b$  and  $u_0$ . With  $p_0 d_0$  as boundary, the Parshen curve is divided into two regions: A and B. When the system works in the region A, the main reaction in the plasma is decomposition. The voltage is used to compensate the energy loss caused by the collisions between the plasma particles and the chamber wall. But when the system works in the region B, the main reaction is phase synthesis and the voltage is used to compensate the energy consumption in the collisions between particles of the plasma [8]. In our system the glow discharge is easy to obtain at a higher voltage. This means that the system works in the region A. Considering the special shape of the deposition zone, it also can be divided into two regions: I and II (as shown in Figure 9). By careful adjustment of the system pressure and the radio frequency we can make region I work at point a which is near  $p_0 d_0$ , therefore plasma will be produced in region I. If we place the substrate in region II, because  $d_2 < d_1$ , according to the Parshen curve the glow discharge voltage  $u_2$  is larger than  $u_1$ ; thus there will be no glow discharge in region II. But if the radio frequency potential  $V_1$  is high causing the region I operating point to shift from point a to a', then region II voltage just satisfies  $V_2 = u_2$  and therefore region II will glow. According to the above analysis we know that the ideal situation in the PECTD systems is that the plasma between the two electrodes works at point a' and therefore the plasma from the sample to the upper electrode works at point b. Because point a' is closer to region B than point b, the synthesis reaction will easily take place in the plasma. Region II which works at point b is suitable for the deposition of GaAs thin film.

4) Some amount of  $H_2$  is directly added to the deposition region during the deposition process. It functions for adjusting the pressure of the system. Furthermore, it also can dispel GaCl gas which can easily absorb water and the corrosive HCl gas. Therefore the quality of sample surface can be improved. But too high  $H_2$  flux will decrease the deposition velocity. /361

It is worth while to mention that the full saturation of a Ga source is not necessary for preparation of a GaAs thin film by PECTD. And such saturation is also very difficult to obtain. This is because the PECTD system is a negative pressure system. In this system  $H_2$  carries AsCl to the source zone and at a certain temperature it will be decomposed into  $As_4$  and HCl gases. Due to the continuous abstraction by the vacuum pump, time is not sufficient to saturate a Ga source by  $As_4$  before entering the deposition zone. HCl gas can only interact with a Ga surface to produce GaCl gas.

## CONCLUSION

1. The results of different characterization methods show that by using AsCl<sub>3</sub> and Ga as reaction sources a GaAs thin film with amorphous structure can be prepared with the PECTD method.

2. The structure and composition of a-GaAs thin films are closely related to the selection and control of the growth conditions. By a strict control of  $T_{so}$ ,  $T_s$ , radio frequency power at the deposition zone, flux of AsCl<sub>3</sub>, etc., an a-GaAs thin film with bright surface, nearly stoichiometric composition, and good reproducibility can be obtained.

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